

Generalized Theory of Electrode Kinetics at Constant Potential

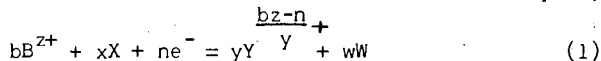
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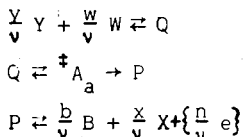
The theory of irreversible electrode reactions at constant potential treats reactions under simultaneous control by charge-transfer and mass-transfer polarization.(1-5) It predicts the current-time curve following an abrupt change in electrode potential from the reversible potential to a new value which is maintained by use of a potentiostat. The treatment assumes that mass transfer occurs by diffusion only; experimentally this condition is closely approached by use of short electrolysis time, of unstirred solutions to minimize convection, and of large excess of supporting electrolyte in the solution to minimize migration of reacting ions in the applied field. Electrodes of planar geometry have been of greatest interest, (1-4) although cylindrical and spherical electrodes have also been treated.(4,5)

All of the previous theory has been limited to first-order charge-transfer mechanisms with the further restriction that the electrical work involved in the reaction occur only during the rate-determining step. The purpose of this paper is to extend the theory to higher-order mechanisms, with removal of the restriction on the electrical work involved. The treatment is for conditions of planar electrode geometry, mass transfer only by semi-infinite linear diffusion, and excess supporting electrolyte. Approximate solutions valid for small concentration changes are derived in closed form.

The general electrode reaction is formulated conventionally (6,7) as



The important reaction steps in the anodic direction are



where P and Q are intermediate states defining the rate-determining step, and v is the stoichiometric number. The total number of electrons (n/v) involved in the decomposition of one mole of the anodic activated complex (${}^{\ddagger}A_a$) is placed in braces to indicate that the number of electrons used up in forming the intermediates P, ${}^{\ddagger}A_a$ or Q is not fixed. Electrical work done during formation of P from the cathodic reactants will be represented by p, and that done in formation of Q from the anodic reactants by q. The net anodic reaction rate at potential ϕ (overpotential η positive) is expressed as current density by (8)

$$i = i_0 \left(\frac{{}^{\ddagger}f_r}{{}^{\ddagger}f} \right) \cdot \exp \left[\frac{(1-\beta)(p_r - p) + \beta(q_r - q)}{RT} \right] \cdot \left\{ \left(\frac{a_Y}{a_O} \right)^{y/v} \left(\frac{a_W}{a_B} \right)^{w/v} \cdot \exp(1-\beta) \frac{n}{v} \epsilon \eta - \left(\frac{a_B}{a_O} \right)^{b/v} \left(\frac{a_X}{a_X} \right)^{x/v} \cdot \exp(-\beta) \frac{n}{v} \epsilon \eta \right\} \quad (2)$$

Here i is the exchange current density, f the activity coefficient of the activated complex, β the transfer coefficient and $\epsilon \equiv F/RT$. The activity of a reactant, e.g. B, is designated a_B in the solution at the electrode surface and a_B^0 in the bulk. Quantities f , p and q refer to the reaction at the applied potential \mathcal{E} and may be time dependent, while the same quantities with subscript r refer to the reaction at the reversible electrode potential \mathcal{E}_r . At the reversible potential the exchange current density is given by

$$i_0 = i_{0,s} \cdot \left[(a_B^0)^b (a_X^0)^x \right]^{(1-\beta)/\nu} \cdot \left[(a_Y^0)^y (a_W^0)^w \right]^{\beta/\nu} \cdot \exp \left[\frac{(1-\beta)(p_s - p_r) + \beta(q_s - q_r)}{RT} \right] \quad (3)$$

where $i_{0,s}$ is the exchange current density at the standard electrode; (7) quantities p_s and q_s also refer to the standard electrode. Equations (2) and (3) have general applicability with one limitation, namely that the activated complex $\ddagger A$ must contain the reactants B and X in the ratio b/x , but this limitation is easily eliminated when desired without introduction of any new principle. (6,7)

It is evident from Eq. (3) that the reaction order, as conventionally determined from i_0 , is not a simple quantity. (7) Thus for substance B:

$$\left(\frac{\partial \ln i_0}{\partial \ln a_B^0} \right)_{T, a_X, a_Y, a_W} = \frac{b(1-\beta)}{\nu} - \frac{1}{RT} \left(\frac{\partial (p_r - \beta p_r + \beta q_r)}{\partial \ln a_B} \right)_{T, a_X, a_Y, a_W} \quad (4)$$

As a general rule, therefore, complex electrode reactions may not be described as being of first order, second order, etc., in the usual manner of chemical kinetics. It is expedient for the theory of combined charge- and mass-transfer polarization to describe the reaction by a pseudoorder, which we define here as simply the exponent of the activity ratio in the general rate equation (Eq. 2). Thus the pseudoorder of the reaction is y/ν with respect to Y, w/ν with respect to W, etc., if each of the reacting substances undergoes changes in concentration during the reaction. If one of the substances involved, e.g. W, exhibits minute fractional changes in concentration during the entire reaction period, the term $(a_W/a_W^0)^{w/\nu}$ becomes unity in Eq. 2 and then the reaction becomes effectively zero pseudoorder in W.

For simplicity we will formulate the electrolyte to contain one of the cathodic reactants, X, and one of the anodic reactants, W, in sufficiently high concentration that the ratios a_X/a_X^0 and a_W/a_W^0 remain essentially unity. In addition, we will consider only short reaction times such that all concentration changes at the electrode surface remain small. From the latter condition plus the use of excess supporting electrolyte, it may be assumed that f/f_r is replaceable by unity and that concentration ratios may be substituted for the corresponding activity ratios with negligible effect. Then Eq. 2 converts to

$$i = i_0 \exp \left[\frac{(1-\beta)(p_r - p) + \beta(q_r - q)}{RT} \right] \cdot \left\{ \left(\frac{c_Y}{c_Y^0} \right)^{y/\nu} \exp(1-\beta) \frac{n}{\nu} \epsilon \eta - \left(\frac{c_B}{c_B^0} \right)^{b/\nu} \exp(-\beta \frac{n}{\nu} \epsilon \eta) \right\} \quad (5)$$

It would be desirable to obtain analytical solutions of the diffusion problem for a current of the form given in Eq. 5 but one cannot apply the method of Laplace transforms. An alternative approach is to obtain an approximate solution by linearizing Eq. 5 with respect to concentrations, so that the Laplace transform

method may be utilized. The latter approach will be developed in this paper. For the sake of brevity we restrict our discussion to cases for which the electrical work occurs only in the rate-determining step, so that $p_1 = p = p_2 = q = 0$. (In general, provided only that p and q are continuous functions of the concentrations, Eq. 5 can always be linearized with respect to concentrations. The form of the approximate solution does not change; however, the coefficients involved become somewhat more complicated.)

It is convenient to introduce the fractional changes in concentration at the electrode surface:

$$u_Y \equiv (c_Y - c_Y^0)/c_Y^0 \quad u_B \equiv (c_B - c_B^0)/c_B^0 \quad (6)$$

Then, for small concentration changes,

$$\left(\frac{c_Y}{c_Y^0}\right)^{y/v} = 1 + \left(\frac{y}{v}\right)u_Y \quad \left(\frac{c_B}{c_B^0}\right)^{b/v} = 1 + \left(\frac{b}{v}\right)u_B$$

and, in the present case ($p=q=0$), Eq. 5 becomes

$$i = i(t=0) + U_Y u_Y - U_B u_B \quad (7)$$

with

$$i(t=0) = i_0 \left[\exp(1-\beta) \frac{n}{v} \epsilon \eta - \exp(-\beta \frac{n}{v} \epsilon \eta) \right] \quad (8)$$

$$i_0 = i_{0,s} \left[(a_B^0)^b (a_X^0)^x \right]^{(1-\beta)/v} \cdot \left[(a_Y^0)^y (a_W^0)^w \right]^{\beta/v}$$

and

$$U_B = \frac{b}{v} i_0 \exp(-\beta \frac{n}{v} \epsilon \eta) \quad ; \quad U_Y = \frac{y}{v} i_0 \exp(1-\beta) \frac{n}{v} \epsilon \eta \quad (9)$$

The diffusion problem: We consider the semi-infinite linear diffusion of two species, B and Y, with concentrations $c_B(x,t)$, $c_Y(x,t)$ coupled together at the electrode surface $x=0$ by a general current-concentration relationship like that of Eq. 5.

$$i(t) = f(c_B(0,t), c_Y(0,t)) \quad (10)$$

The diffusion equations for c_B and c_Y are

$$D_B \frac{\partial^2 c_B}{\partial x^2} = \frac{\partial c_B}{\partial t} \quad ; \quad D_Y \frac{\partial^2 c_Y}{\partial x^2} = \frac{\partial c_Y}{\partial t} \quad (11)$$

where D_B and D_Y are the diffusion coefficients of substances B and Y. The initial conditions are $c_B = c_B^0$ and $c_Y = c_Y^0$ at $t=0$ for all x . The boundary conditions are

$$(1) \quad c_B \rightarrow c_B^0 \text{ and } c_Y \rightarrow c_Y^0 \text{ as } x \rightarrow \infty \text{ for all } t \quad (12)$$

$$(2) \quad i(t) = \frac{nF}{Y} D_Y \left(\frac{\partial c_Y}{\partial x} \right)_{x=0} = - \frac{nF}{b} D_B \left(\frac{\partial c_B}{\partial x} \right)_{x=0} = f[c_B(0,t), c_Y(0,t)] \quad (13)$$

When the current, $i(t)$, contains non-linear terms in the concentrations the complete solution to the problem of Eq. 11-13 cannot be obtained by standard analytic techniques. However, a useful relationship, valid for any functional

dependence of $i(t)$ upon the concentrations, can be found by applying the Laplace transform technique to Eq. 11-13 as they stand.

To obtain this relationship we require only that $i(t)$ be some arbitrary (and, indeed, at this point unknown) function of the time whose Laplace transform exists. Then a straightforward application of the Laplace transform technique yields the relation

$$\frac{c_B(x=0,t) - c_B^0}{c_Y(x=0,t) - c_Y^0} = \frac{b}{y} \sqrt{\frac{D_Y}{D_B}} \quad (14)$$

The principal utility of Eq. 14 is that it permits the diffusion problem to be solved in terms of just one of the components B and Y. In the actual expression for the current in terms of concentrations at the electrode surface (see Eq. 10), we eliminate $c_B(x=0,t)$ by using Eq. 14 and are left with a diffusion problem for component Y in which component B plays no part whatsoever.

However, although Eq. 14 simplifies the diffusion problem to one involving the diffusion of only one component (Y, say), it does not remove the generally non-linear dependence of current on concentration, and recourse must be had either to numerical solutions or to an approximate solution based on the linearized form of Eq. 7.

In this linearized form, and with component B eliminated via Eq. 14, the diffusion problem is expressed in terms of the fractional change in concentration $u_Y(x,t)$ (Eq. 6) as

$$D_Y \frac{\partial^2 u_Y}{\partial x^2} = \frac{\partial u_Y}{\partial t} \quad (15)$$

with

$$u_Y(x,t=0) = 0, \quad u_Y(x \rightarrow \infty, t) \rightarrow 0 \quad (16)$$

and the conditions on the current:

$$i(t) = \frac{n}{y} F c_Y^0 D_Y \left(\frac{\partial u_Y}{\partial x} \right)_{x=0} \quad (17)$$

$$i(t) = i(t=0) + u_Y(x=0,t) \left[u_Y + \left(\frac{b c_Y^0 \sqrt{D_Y}}{y c_B^0 \sqrt{D_B}} \right) u_B \right]$$

The solution of Eq. 15-17 is found by Laplace transform techniques to be

$$i = i(t=0) \exp(\lambda^2 t) \operatorname{erfc}(\lambda \sqrt{t}) \quad (18)$$

$$c_Y = c_Y^0 - i(t=0) \left[\frac{n}{y} F \lambda \sqrt{D_Y} \right]^{-1} \cdot [1 - \exp(\lambda^2 t) \operatorname{erfc}(\lambda \sqrt{t})] \quad (19)$$

$$c_B = c_B^0 + i(t=0) \left[\frac{n}{b} F \lambda \sqrt{D_B} \right]^{-1} \cdot [1 - \exp(\lambda^2 t) \operatorname{erfc}(\lambda \sqrt{t})] \quad (20)$$

where

$$\lambda = \frac{u_Y}{(n/y) F c_Y^0 \sqrt{D_Y}} + \frac{u_B}{(n/b) F c_B^0 \sqrt{D_B}} \quad (21)$$

which, on substituting for U_Y and U_B from Eq. 9, becomes

$$\lambda = \left(\frac{y}{v}\right)^2 \frac{i_0 \exp(1-\beta) \frac{n}{v} \epsilon \eta}{F c_Y^0 \sqrt{D_Y}} + \left(\frac{b}{v}\right)^2 \frac{i_0 \exp(-\beta \frac{n}{v} \epsilon \eta)}{F c_B^0 \sqrt{D_B}} \quad (22)$$

This equation and Eq. 18-20 reduce to the corresponding equations for first-order reactions (2,4) when $b=y=v=1$.

Thus the approximate solution for charge-transfer reactions of higher order has the same form as the exact solution for simple first-order reactions. (2,4) The major difference lies in the quantity λ . According to Eq. 18 the larger the value of λ the more rapidly the relative current $i/i(t=0)$ decreases with time. The evaluation of the quantities λ and $i(t=0)$ from an experimental current-time curve can be carried out using methods previously developed for simple first-order reactions. (2,4,9) The charge-transfer parameters i_0 , β and v can then be found either from measurement of the anodic or cathodic Tafel line in the case of slow reactions or from measurements of $i(t=0)$ for varying activity of B or Y in the case of faster reactions.

Validity of approximate solution: The approximate solution given by Eq. 18-21 is valid only for small changes in concentration; its utility is chiefly determined by the range over which it gives the true current to within an acceptable accuracy. In order to test this we have developed exact numerical solutions using the Schmidt method, (10). Some of these exact current-time curves for net anodic reactions are presented in Fig. 1: curve I refers to a simple first-order reaction for which $b/v = y/v = n/v = 1$; curve II refers to a reaction second pseudoorder in the anodic reactant Y with $y/v = n/v = 2$ and $b/v = 1$; curve III refers to a reaction third pseudoorder in Y, with $y/v = n/v = 3$. The set of numerical data used here is the same as in the previous paper: (4) $i_0 = 5 \times 10^{-3}$ A/cm² at 25°C, $\beta = 0.5$, $\eta = 0.0100V$; $c_Y = 10^{-5}$ and $c_B = 5 \times 10^{-5}$ mole/cm³; $D_Y = 10^{-5}$ and $D_B = 2 \times 10^{-5}$ cm²/s. Fig. 1 shows that, as the reaction pseudoorder in Y is increased, the current falls more rapidly with time.

The approximate and exact solutions for reactions of second pseudoorder in Y are shown in Fig. 2 for various values of the transfer coefficient β ; except for β the set of numerical data employed is the basic set used for Fig. 1. It is seen that in every case the approximate solution for the current decreases more rapidly with time than does the true current.

We have chosen to designate the range in $i/i(t=0)$ over which Eq. 18 gives satisfactory agreement with the true current by the point at which the approximate solution deviates by 5% from the true current. These points are indicated by vertical bars in Fig. 2; the approximate solution is acceptably accurate down to $i/i(t=0) \approx 0.45$, independent of the value of β . As Oldham and Osteryoung (9) have emphasized, the reaction kinetics are primarily diffusion controlled below $i/i(t=0) \approx 0.5$. Thus, in this case, the approximate solution (eq. 18) is acceptably accurate over the entire range in $i/i(t=0)$ from which information about the charge-transfer parameters can be obtained.

For a reaction third pseudoorder in the anodic reactant Y the approximate and exact solutions are compared in Fig. 3. The numerical data are the basic set used for Fig. 1, with $\beta = 0.5$ and $y = 3$. The range in $i/i(t=0)$ over which acceptable agreement is found is shorter than that for the similar second pseudoorder reaction: the point of 5% deviation occurs at $i/i(t=0) \approx 0.6$.

The agreement to be expected for somewhat slower reactions is shown in Fig. 4. Here the basic data set was varied by increasing the anodic overpotential to $\eta = 0.1$ V and decreasing the exchange current density to $i_0 = 10^{-5}$ A/cm². The limits of acceptable agreement are indicated by vertical bars. In this case the point of 5% deviation occurs at $i/i_0(t=0) \approx 0.61$ and is again essentially independent of the value of the transfer coefficient β .

Thus far we have examined only net anodic reactions in which the higher pseudoorder component was the anodic reactant (Y). In these cases, because of the disparity of the exponential factors in Eq. 5, the current is predominantly controlled by the higher pseudoorder component, this predominance becoming greater the greater the overpotential. This is the reason for the poorer agreement shown in Fig. 4 ($\eta = 0.1$ V) than in Fig. 2 ($\eta = 0.01$ V).

The agreement between the approximate and exact numerical solutions improves dramatically when the controlling reactant is the first order reactant (for example, a net anodic reaction in which the higher pseudoorder component is the cathodic reactant (B)). This is illustrated in the anodic current-time curves of Fig. 5, for which the values of temperature, diffusivities and initial concentrations are those of the basic data set. Curve II, for which the cathodic reactant (B) is second pseudoorder while the anodic reactant (Y) is first order, shows no measurable deviation between the approximate and exact solutions down to $i/i_0(t=0) < 0.2$.

These examples suggest some general rules about the range of validity of the approximate solution:

- (1) The range of validity decreases when the pseudoorder of either component is increased.
- (2) The range of validity is extended greatly by ensuring that the current is predominantly controlled by the component of lower pseudoorder. If, for example, the higher order component is the cathodic component then a net anodic reaction is desirable.
- (3) If rule (2) has been complied with there is an advantage in working at the highest feasible overpotentials. If not, the advantage is obtained by working at the lowest feasible overpotentials.
- (4) The range of validity is insensitive to the value of the transfer coefficient β .

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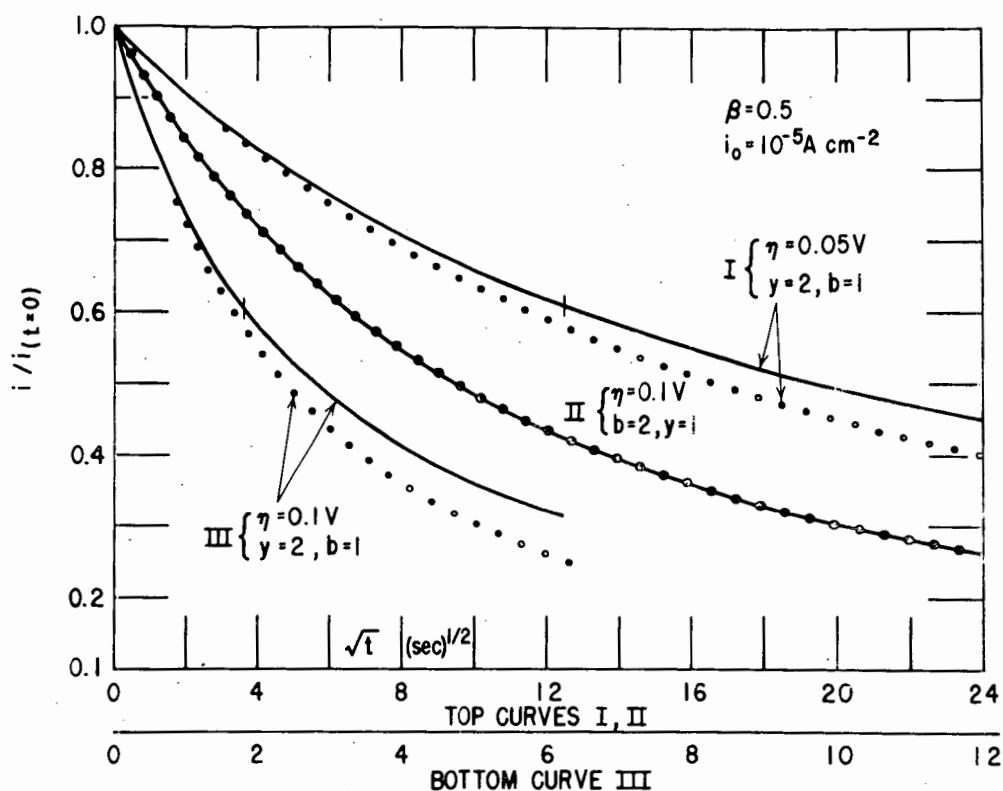


FIG. 5--ANODIC CURRENT-TIME CURVES FOR REACTIONS OF PSEUDOORDER TWO WITH RESPECT TO ANODIC REACTANT Y (CURVES I, III) OR CATHODIC REACTANT B (CURVE II). SOLID CURVE--EXACT NUMERICAL SOLUTION. DOTTED CURVE--SOLUTION OF LINEARIZED PROBLEM.

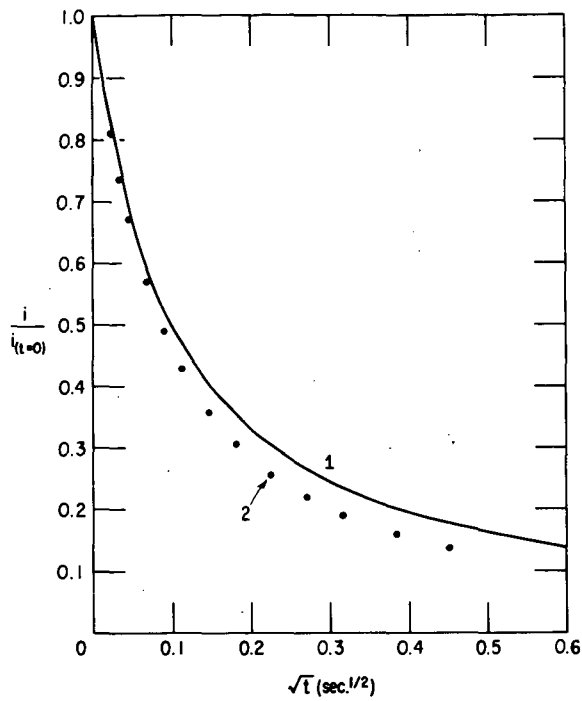


FIG. 3 CURRENT-TIME BEHAVIOR FOR REACTION OF PSEUDOORDER THREE WITH RESPECT TO Y. CURVE 1-EXACT NUMERICAL SOLUTION; 2-SOLUTION OF LINEARIZED PROBLEM.

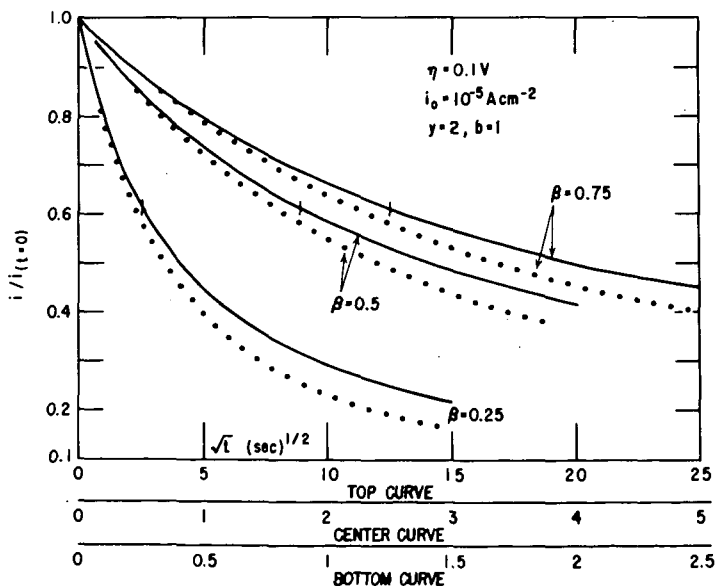


FIG. 4--EFFECT OF β ON ANODIC CURRENT-TIME CURVES FOR REACTION OF PSEUDOORDER TWO WITH RESPECT TO ANODIC REACTANT Y. SOLID CURVES--EXACT NUMERICAL SOLUTION. DOTTED CURVES--SOLUTION OF LINEARIZED PROBLEM.

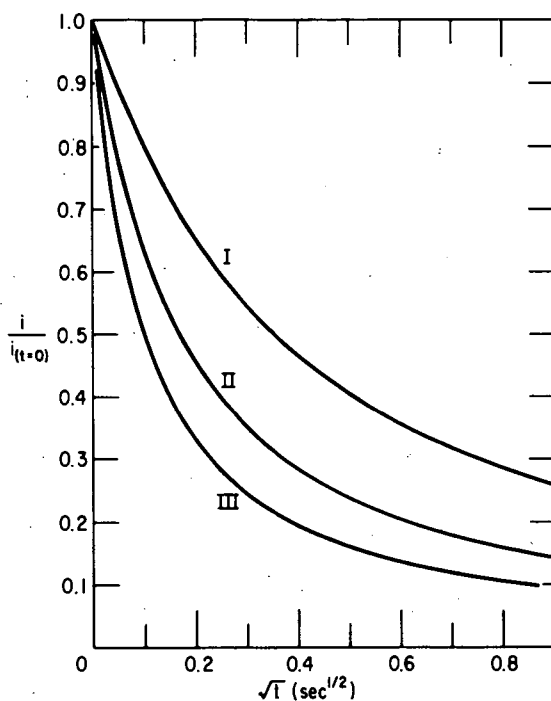


FIG. 1 EXACT CURRENT-TIME BEHAVIOR FOR SELECTED ELECTRODE REACTIONS OF PSEUDOORDER ONE (CURVE I), TWO (II) OR THREE (III) WITH RESPECT TO SUBSTANCE Y.

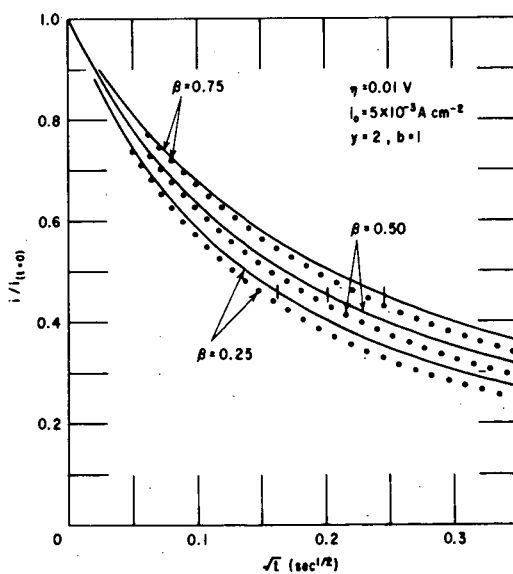


FIG. 2--EFFECT OF β ON ANODIC CURRENT-TIME CURVES FOR REACTION OF PSEUDOORDER TWO WITH RESPECT TO ANODIC REACTANT Y. SOLID CURVES--EXACT NUMERICAL SOLUTION. DOTTED CURVES--SOLUTION OF LINEARIZED PROBLEM.